

学校编码: 10384

分类号_____密级_____

学号: 19120051403076

UDC _____

廈門大學

博 士 学 位 论 文

CoPt 和 NiPt 合金纳米催化剂: 合成、自组装及其电催化和异常红外性能

**CoPt and NiPt Alloy Catalysts: Preparation, Self-Assembly,
Electrocatalytic and Anomalous IR Properties**

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论文提交日期: 2008 年 11 月

论文答辩时间: 2008 年 12 月

学位授予日期: 2008 年 月

答辩委员会主席: _____

评 阅 人: _____

2008 年 11 月

**CoPt and NiPt Alloy Catalysts: Preparation, Self-Assembly,
Electrocatalytic and Anomalous IR Properties**



A Dissertation Submitted for the Degree of Doctor Philosophy

By

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2008

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摘 要

纳米材料具有不同于常规材料的特殊性质，在科学技术的发展中具有重要地位。纳米材料的合成，尤其是形状和结构控制合成、纳米材料的表征及其特殊性能的研究是纳米材料科学的前沿课题。CoPt 和 NiPt 纳米材料由于其独特的磁学性能、高效的催化性能和特殊的光学性能而备受关注。本论文运用化学还原和电位置换法制备了不同结构的 CoPt 和 NiPt 纳米粒子，系统研究了它们的磁学、电催化和特殊红外光学性能。主要研究内容和结果如下：

(1) 一维链状 CoPt 纳米材料的合成及其性能研究。运用化学还原和电位置换法制备了两种不同结构的一维链状 CoPt 纳米材料，其一为实心结构(CoPt-a)，另一种为空心结构(CoPt-b)。磁性研究指出，CoPt-a 和 CoPt-b 纳米材料均表现出超顺磁性，对应的阻塞温度 T_B 分别为 10.0 K 和 9.0 K。5 K 时测得矫顽力分别为 520 Oe 和 740 Oe；电化学循环伏安结果给出，CoPt-a/GC 和 CoPt-b/GC 纳米粒子电极对 CO 的氧化都具有较好的电催化活性。与本体 Pt 电极相比，CO 氧化峰电位分别提前了 140 mV 和 160 mV。还测得 CoPt-b 纳米粒子对甲醇氧化具有很高的电催化活性，其氧化电流密度是商业 Pt/C 催化剂的 1.9 倍，稳定性与商业 Pt/C 催化剂相当。根据实验结果，CoPt-b 纳米粒子对甲醇氧化有较好的催化活性可归因于 Co 元素的协同作用和其特殊的空心结构。原位红外光谱结果表明，当 CoPt-a 和 CoPt-b 纳米粒子负载在中等反射率的 GC 基底或高反射率的 Au 基底上时，无论是在固/液界面还是固/气界面，吸附态 CO 均给出异常红外效应(AIREs)的光谱特征。不同反射率的基底会影响增强红外吸收强度、半峰宽、Stark 系数等参数，但不会改变 AIREs 光谱特征。进一步证明 AIREs 是一维 CoPt 纳米材料本身的特性，与基底无关。首次观察到一维纳米材料同样具有异常红外效应。研究结果有助于深入认识低维纳米材料异常红外性能的本质。

(2) 单分散 NiPt 纳米粒子合成及其性能研究。首次将电位置换法成功地应用到较难合成的 NiPt 体系，制备了单分散的 NiPt 纳米粒子。在实验的基础上，提出了合成机理。结果指出，实验体系的温度、反应物的滴加顺序和反应物比例是决定产物组成和结构的关键因素。NiPt 纳米粒子同样表现出超顺磁性行为，测得阻塞温度 T_B 为 7.8 K，5 K 时矫顽力为 517 Oe；原位红外光谱研究结果给出，在固/液界面和固/气界面、在中等反射率的 GC 基底和高反射率的 Au 基底上获得的结果光谱和单光束光谱中，吸附在 NiPt 纳

米粒子上的 CO 均给出类 Fano 红外效应特征。同时表现出很强的红外增强吸收,测得在 GC 基底和 Au 基底上的红外增强因子分别为 73 和 112。本研究首次在化学法合成的单分散 NiPt 纳米粒子上观察到类 Fano 红外效应,进一步验证了类 Fano 红外效应同样是低维纳米材料特殊的红外光学性能,对深入认识低维纳米材料特殊红外性能本质亦具有重要价值。

(3) 空心结构 NiPt 和 CoPt 纳米粒子对甲醇电催化氧化性能研究。首次运用电位置换法和共还原法得到空心结构(NiPt-a)和实心结构(NiPt-b)纳米粒子。电化学循环伏安研究结果指出, NiPt-a 纳米粒子对甲醇氧化具有很高的电催化活性,其氧化电流密度是商业化 Pt/C 催化剂的 1.9 倍,同时具有较好的稳定性。NiPt 纳米粒子对甲醇氧化有较好催化活性主要归因于双功能机理,也与纳米粒子的化学效应、电子效应及其特殊的空心结构相关联。运用原位红外光谱在分子水平研究了空心结构 CoPt 和 NiPt 纳米粒子上甲醇的电化学氧化过程。在空心结构 CoPt 纳米粒子上,检测到毒性中间体 CO 及其给出的异常红外效应光谱特征;而在空心结构 NiPt 纳米粒子上观察到类 Fano 红外效应,与直接用 CO 做为分子探针得到的结果一致。空心结构纳米粒子具有较高的催化活性,同时能提高金属催化剂利用率。因此,研究结果对发展燃料电池新型 Pt 基纳米催化剂具有指导意义。

(4) 核壳结构 CoPt@Pt 纳米粒子的合成、自组装及其红外光学性能研究。运用改进的化学还原和电位置换法得到了 CoPt 纳米粒子,以 HRTEM、XPS、XRD 等方法表征确认制备的纳米粒子为核壳结构。通过液/液界面自组装得到 CoPt@Pt 纳米粒子单层薄膜。透射红外光谱结果指出,吸附态 CO 在单分散无序堆积的 CoPt₄/Si 上给出增强红外吸收,而在纳米粒子薄膜 CoPt_a/Si 上给出类 Fano 红外效应。在 CoPt_a/Si 上吸附态 CO 的谱峰强度比在 CoPt_d/Si 上增强了约 5 倍。研究结果为合成核壳结构纳米粒子提供了一种新方法,进一步发展了液/液界面自组装方法。

本论文研究结果对深入认识 CoPt 和 NiPt 纳米粒子的特殊性能,探索低维纳米材料特殊红外性能的本质具有重要意义,同时对研制直接甲醇燃料电池新型电催化剂具有重要应用价值。

关键词: CoPt, NiPt 合金纳米粒子; 液/液界面自组装; 电催化; 异常红外性能

Abstract

Synthesis, especially the controlled synthesis, characterization and properties of nanomaterials are the most important tasks in nanoscience because they have unusual properties that could not be possessed by corresponding bulk materials. CoPt and NiPt nanomaterials have attracted multidisciplinary attentions because of their special magnetic, catalytic and optical properties. In this paper, CoPt and NiPt nanomaterials with different structure were prepared by chemical reduction and galvanic displacement reaction, and their magnetic, electrocatalytic and anomalous IR properties were studied. The main experiments and results are given as follow:

(1) Synthesis and properties of one-dimension (1D) chain-like CoPt nanomaterials. Two kinds of 1D CoPt nanomaterials were prepared by galvanic displacement reaction. One is a solid structure (CoPt-a), the other is a hollow structure (CoPt-b). The results of magnetic measures showed that both CoPt-a and CoPt-b are superparamagnetic. The blocking temperatures of CoPt-a and CoPt-b are 10.0 K and 9.0 K. The coercivities are 520 Oe and 740 Oe obtained at 5 K, respectively. The results of CV demonstrated that the 1D chain-like CoPt-a and CoPt-b nanomaterials exhibit better electrocatalytic properties for CO oxidation than that of bulk Pt does in 0.1 M H₂SO₄. The current peak potentials of CO oxidation are shifted negatively by 140 mV and 160 mV comparison with bulk Pt electrode, respectively. It is clearly that the catalytic activity of the hollow CoPt-b nanoparticles is much higher than that of commercial Pt/C catalyst for electrooxidation of methanol. The oxidation density on CoPt-b nanoparticles is nearly 1.9 times than that on Pt/C catalyst. The remarkably high activity of CoPt-b nanomaterials may come from the effect of the cooperating function of Co element and the special hollow structure. The fact that both CoPt-a and CoPt-b nanomaterials loaded on GC or Au substrates produce abnormal infrared effects (AIREs) has confirmed that the anomalous IR features were generated mainly by the 1D chain-like CoPt nanomaterials, and that the influence of the substrate materials on the IR spectral features may be neglected in the present study. The current study demonstrated that 1D nanomaterials also show AIREs

for the first time, and thrown a new insight into understanding the origin of anomalous IR properties observed on low-dimensional nanomaterials.

(2) Synthesis and properties of monodispersed NiPt nanomaterials. Galvanic displacement reaction was introduced to synthesize monodispersed NiPt nanoparticles successfully for the first time. The size, composition and morphology can be well controlled by varying reaction temperature and ratio of the reactants. A probable mechanism for the formation of the NiPt nanoparticles was proposed based on a series of assistant experiments. The obtained NiPt nanoparticles are superparamagnetic too. The blocking temperature is 7.8 K with a coercivity of 517 Oe at 5 K. *In situ* electrochemical FTIRS employing CO adsorption as probe reaction demonstrated that NiPt/GC or NiPt/Au electrodes exhibit characteristics of Fano-like infrared effects either in result spectra or single spectra. The substrate materials do not affect significantly the anomalous IR features, as illustrated by the similar anomalous IR features observed for CO adsorbed on both NiPt/GC and NiPt/Au electrodes. The results demonstrated that dispersed NiPt nanomaterials obtained by chemical method display characteristics of Fano-like infrared effects for the first time, and are of significant academic importance in understanding the origin of anomalous IR properties observed on low-dimensional nanomaterials.

(3) Properties of methanol electrooxidation of CoPt and NiPt nanomaterials with a hollow structure. Two kinds of NiPt nanomaterials were prepared by galvanic displacement reaction. One is a hollow structure (NiPt-a), the other is a solid structure (NiPt-b). The results of CV demonstrated that the electrocatalytic activity of NiPt-a nanoparticles is much higher than that of commercial Pt/C catalyst for the electrooxidation of methanol. The oxidation density on NiPt-a nanoparticles is nearly 1.9 times than that on Pt/C catalyst. The remarkably high activity of the NiPt nanomaterials for oxidation of methanol may come from the bifunctional mechanism, electron effect, chemical effect and the special hollow structure of the nanomaterials. The electrooxidation of methanol on CoPt-b and NiPt-a nanoparticles was studied on the molecular level by *in situ* FTIR. The poisonous intermediates CO observed on CoPt-b/GC electrode displays AIREs while shows Fano-like infrared effects on NiPt-a/GC electrode. The results are of significant academic importance in developing catalysts of fuel cell.

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